AD-A008 971

KINETICS OF FLUORINE REACTIONS

Joseph B. Levy

George Washington University

Prepared for:

Air Force Office of Scientific Research

February 1975

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR - TR - 75 - 0598	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD-A008971
4. TITLE *(and Subtitle)* KINETICS OF FLUORINE REACTIONS		5. TYPE OF REPORT & PERIOD COVERED Final 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Joseph B. Levy		8. CONTRACT OR GRANT NUMBER(s) AFOSR-70-1939
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry George Washington University Washington, D.C. 20052		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 9750-02, 61102F, 681308
11. CONTROLLING OFFICE NAME AND ADDRESS AF Office of Scientific Research/NC 1400 Wilson Boulevard Arlington, Va. 22209		12. REPORT DATE February 1975 13. NUMBER OF PAGES 5 7
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Fluorine Kinetics Enthalpy and entropies Bond dissociation energies
Perfluorocyclobutane
Bistrifluoromethyl peroxide Trifluoromethyl hypofluorite

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report covers research done from September 1, 1970 to November 30, 1974. Four publications resulted. The research focussed on the chemistry of fluorine and its compounds. One system studied was the equilibrium of CF3OOCF3 with CF3OF plus COF2. Equilibrium constants, forward and reverse reaction rates and the standard enthalpy and entropy for this system were determined. The bond dissociation energy for the O-O bond in bistrifluoromethyl peroxide and for the O-F bond in trifluoromethyl hypofluorite were determined. The study of the fluorine with perfluorocyclobutane reaction system was also completed. This

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

This research has covered the period September 1, 1970 through September 1, 1974. The principal investigator for this period has been Professor Joseph B. Levy and the research associate has been Dr. R. Craig Kennedy.

The focus of the research has been on the chemistry of fluorine and its compounds. The unique nature of fluorine manifests itself in the high reactivity of the element itself and in the interesting and unusual properties that fluorine imparts to compounds when it is incorporated in them. Both of these aspects are pertinent to the interests of the U.S. Air Force in that fluorine itself and fluorine-containing compounds are capable of acting as ingredients of high energy propellants on the one hand, and also yield lubricants, insulators, etc. of great chemical inertness on the other hand. We believe we can make the modest assertion that the research described here has added significantly to our knowledge of the chemistry of this element.

The research covered in this program falls rather naturally into two parts. Three publications have resulted from this work and the manuscript of a fourth, which will be submitted for publication, is attached. The first part of the research dealt with the interesting equilibrium:

$$CF_3OOCF_3 \rightleftarrows CF_3OF + COF_2$$

Our first and second publications, of which copies are attached, describe studies of this equilibrium. They illustrate rather profound effects of fluorine substitution. The first paper describes measurements of the thermodynamic properties of the above system. It is interesting that the corresponding reaction for the hydrogen analog:

$$CH_3OOCH_3 \rightarrow CH_3 + CH_2O$$

is not an equilibrium, but an irreversible reaction. The particular nature of fluorine, among others, the relative weakness of its bond to oxygen, results in a reversible nature to the reaction which in turn leads to a particular stability of the perfluorinated peroxide since it has no easy route to destruction. A second effect of fluorine, illustrated in the above case, is its effect on other bonds in molecules in which it is incorporated. In the above case the result is a substantially increased oxygen-oxygen bond in the peroxide. In the second paper this effect is documented and its origin discussed.

The third published paper and the manuscript attached describe the second phase of our research. This has been involved with the little-studied homolytic bimolecular substitution reaction, designated S_H2. A consequence of the strong bond that fluorine forms to carbon and the weak one that it forms with itself is that the reaction of fluorine with fluorocarbons is peculiarly well-suited to the study of S_H2 reactions. Our third publication describes what we feel is the only thoroughly studied example of such a reaction outside of studies with three-membered rings and we feel it clarifies effectively the nature of the barriers to such reactions while pointing the way to further points of attack on this problem. The manuscript attached describes an extension of this general area to the system. Here aspects of the chemistry of difluorocarbene were also clarified.

The utility of any program of basic research can only be evaluated in the way in which it contributes to the general body of scientific knowledge. Such an evaluation, in most cases, can only be properly made after some time interval has passed after the research has been completed. One goal that anyone in basic research can set is that whatever results he produces must be reliable and trustworthy, i.e. that his experiments must be well-designed and carefully carried out. That goal has been in the forefront of our minds

as we have proceeded through this research and we feel we have achieved it.

A further aspect of any program of the above sort is the effect it has had on its participants. In the present case the principal investigator has certainly benefitted from his association with the research associate and has been strengthened in his background in fluorine chemistry. He also feels that the research associate, who is now exercising his considerable skills in the service of the Los Alamos Scientific Laboratory has had his understanding of chemical kinetics and theory expanded. The graduate students who have worked in proximity with the research associate have also benefitted.

Finally the principal investigator wishes to acknowledge his debt to Dr. Joseph F. Masi in particular and to Lt. Colonel Richard Haffner, Captain Robert Lawrence and Major David Olson for their help and encouragement in this work.

List of Publications Resulting from Grant No. AFOSR 70-1939

1. "Bistrifluoromethyl Peroxide. I. Thermodynamics of the Equilibrium with Carbonyl Fluoride and Trifluoromethyl Hypofluorite," J. B. Levy and R. C. Kennedy, J. Am. Chem. Soc., 94, 3302 (1972).

2. "Bistrifluoromethyl Peroxide. II. Kinetics of the Decomposition to Carbonyl Fluoride and Trifluoromethyl Hypofluorite," R. C. Kennedy and J. B. Levy, J. Phys. Chem., 76, 3480 (1972).

3. "Homolytic Displacements on Carbon. I. The Fluorine-Perfluorocyclobutane Reaction", J. B. Levy and R. C. Kennedy, J. Am. Chem. Soc., 96, 4791 (1974).

4. "The Pyrolysis of Hexafluoropropylene Oxide", J. B. Levy and R. C. Kennedy, to be submitted for publication.